

A THEORETICAL ANALYSIS OF PREMIXED FLAME PROPAGATION WITH AN  
ISOTHERMAL CHAIN REACTION \*

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A B S T R A C T

An asymptotic analysis, for large activation energies, is presented of the structure of a deflagration wave supported by a two step chemical reaction mechanism with a first order chain-branching reaction and a second order chain termination reaction. In the first step the initial reactant is transformed, without liberation of heat, into an intermediate species; the reaction is auto-catalytic and has a large activation energy. In the second step the intermediate species recombines, with liberation of heat, to give the final products.

Three main regimes are found in the analysis: In a first regime, for very large recombination rates, the steady-state assumption for the intermediate species yields an overall reaction and a corresponding overall reaction rate with a large activation energy. In a second regime, the recombination reaction, takes place everywhere in the flame; the conversion of the initial reactant into the intermediate species occurs in a thin reaction region embedded in the much thicker recombination region. For low recombination rates, an isothermal chain reaction flame precedes a much thicker recombination region where transport effects may be neglected.

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# 1. INTRODUCTION AND FORMULATION

Zeldovich (1948) formulated the flame propagation problem for an idealized chain reaction. He considered in his model that, in a first step, the initial reactant "a" is transformed into an intermediate radical "b" by means of a first order autocatalytic reaction:  $a + b \rightarrow 2b$ . In this first step the overall reaction rate has a large activation energy  $E$  and the heat release is zero. In a second step the intermediate species  $b$  recombines into the final products with liberation of heat:  $b + b \rightarrow \text{Prod.}$  The reaction rate of this second step has a zero temperature dependence and is second order with respect to  $b$ .

This kinetic scheme was introduced by Zeldovich as a simplified model of many chemical reactions, like the  $H_2$ -air reaction.

If the diffusivities of mass and heat  $D$  are assumed to be equal and the specific heat  $c$ , as well as the product  $\rho D$  of density  $\rho$  and  $D$ , is taken as constant, the conservations equations for this deflagration process, may be written in nondimensional form as

$$\frac{d\alpha}{d\xi} - \frac{d^2\alpha}{d\xi^2} = -\Lambda_1 \alpha \beta \exp(-E/RT) \quad (1)$$

$$\frac{d\beta}{d\xi} - \frac{d^2\beta}{d\xi^2} = \Lambda_1 \alpha \beta \exp(-E/RT) - \Lambda_2 \beta^2 \quad (2)$$

$$\frac{d\theta}{d\xi} - \frac{d^2\theta}{d\xi^2} = \Lambda_2 \beta^2 \quad (3)$$

where  $\alpha$  and  $\beta$  are the mass fractions  $a$  and  $b$  divided by the initial mass fraction  $a_0$  of  $a$ . The non-dimensional flame parameter  $\Lambda_2 = B_2 a_0 \rho D / m^2$  is obtained in terms of the reaction constant  $B_2$ , of the reaction rate of the second step,  $B_2 b^2$ , and the mass flux  $m = \rho u$  through the deflagration wave;  $\Lambda_1 / \Lambda_2 = B_1 / B_2$  where  $B_1$  is the pre-exponential factor in the reaction rate,  $B_1 a b \exp(-E/RT)$ , of the first reaction. The temperature has been written in non-dimensional form as  $\theta = cT / ha_0$ , and the distance through the flame  $x$  has been written as  $x = (\rho D / m) \xi$ .

The boundary conditions for the system of Eq.(1) to (3)

are

$$\xi \rightarrow -\infty : \quad \alpha = 1 \quad , , \quad \beta = 0 \quad , , \quad \theta = \theta_0 \quad (4)$$

$$\xi \rightarrow \infty : \quad \alpha = 0 \quad , , \quad \beta = 0 \quad , , \quad \theta = \theta_1 \quad (5)$$

The following relations may be easily obtained from the above system of equations,

$$\alpha + \beta + \theta = 1 + \theta_0 = \theta_1 \quad (6)$$

which may substitute one of the differential equations (1) to (3). These equations may be further reduced to a system of two differential equations, one first order and the other second order by



using, for example,  $\beta$  and  $d\theta/d\xi$  as dependent and  $\theta$  as independent variables. However, we shall operate in the original variables, for reasons of physical clarity in the presentation.

Our purpose is to examine the asymptotic structure of the flame propagation process for large values of the ratio of activation temperature  $E/R$  and final flame temperature  $T_1 = T_0 + h/a_0 c$ . We shall cover in our analysis the complete range of values of the ratio  $\Lambda_1/\Lambda_2 = B_1/B_2$ , from zero to infinity. We shall see that by increasing this ratio from zero to infinity we pass from a regime

- 1) in which the reaction mechanism reduces to an overall reaction, because a steady state assumption for the species  $b$  is applicable, to
- 2) a second regime in which the species  $a$  is converted into  $b$  in a thin reaction zone, embedded in a thick reaction zone where  $b$  is recombined into products, and finally for a sufficiently high value of the ratio  $B_1/B_2$ ,
- 3) a regime exists for which the mode of flame propagation is that due to an isothermal chain as quoted by Zeldovich (1948).

Of course intermediate transition regimes exist between the three ones mentioned above.

Fig.1 shows an schematic representation of the concentration and temperature profiles for the three regimes.

## 2. FAST RECOMBINATION REACTION

If  $\Lambda_2/\Lambda_1 \gg \exp(-E/RT_1)$  the quasi-steady state approximation may be used for the intermediate species b, so that

$$\beta \ll 1 \quad , , \quad \beta = (\Lambda_1/\Lambda_2)\alpha \exp(-E/RT) \quad (7)$$

$$\text{therefore } \alpha + \theta = \theta_1 \quad (8)$$

and

$$\frac{d\theta}{d\xi} - \frac{d^2\theta}{d\xi^2} = \Lambda_2^{-1} \Lambda_1^2 (\theta_1 - \theta)^2 \exp(-2E/RT). \quad (9)$$

The last equation is to be integrated with the boundary conditions

$$\theta(-\infty) = \theta_0 \quad , , \quad \theta(+\infty) = \theta_1 \quad (10)$$

The asymptotic solution of (9) for large values of  $2E/RT$ , may be easily obtained by using the inner and outer expansions method.

A thick transport region where  $\theta$  is given in the first approximation by

$$\frac{d\theta}{d\xi} - \frac{d^2\theta}{d\xi^2} = 0 \quad (11)$$

precedes the thin reaction zone region, located around  $\xi = 0$ ,

where  $\theta$  is given, in the first approximation by

$$\frac{d^2\theta}{d\xi^2} = -\Lambda_2^{-1}\Lambda_1^2 \exp(-2E/RT_1)(\theta_1 - \theta)^2 \exp\{2E(\theta - \theta_1)/RT_1^2\} \quad (12)$$

The solution of (11) is written as

$$\theta = \theta_0 + \exp \xi \quad (13)$$

From (12) we deduce, if  $\theta(\infty) = \theta_1$ ,

$$(d\theta/d\xi)^2 = 2\Lambda_2^{-1}\Lambda_1^2(RT_1^2/2E)^3 \exp(-2E/RT_1)\{2 - (\psi^2 + 2\psi + 2)e^{-\psi}\} \quad (14)$$

where  $\psi = 2E(\theta_1 - \theta)/RT_1^2$ . The matching conditions between (13) and (14) yield

$$\Lambda_2^{1/2}(B_1/2B_2)(RT_1/E)^{3/2} \exp(-E/RT_1) = 1 \quad (15)$$

which determines the flame propagation velocity in the first approximation. Higher order terms in the asymptotic expansion may be calculated without major difficulties.

### 3. INTERMEDIATE RECOMBINATING RATES

If  $\exp(-E/RT_0) \ll \Lambda_2/\Lambda_1 \ll \exp(-E/RT_1)$  it is clear that for an intermediate temperature  $T_2$  the rates of the chain branching and recombining reactions will be equal. That is

$$\Lambda_2/\Lambda_1 = \exp(-E/RT_2) = B_2/B_1 \quad (16)$$

Then, for  $E/RT_2 \rightarrow \infty$  and  $T > T_2$  the first reaction will be in equilibrium, that is  $\alpha = 0$ , and for  $T < T_2$  the first reaction will be frozen. If we take  $\xi = 0$  as the location where, in the asymptotic limit,  $T = T_2$ , then, the system of equations (1) to (3) take the form:

$$\xi < 0 \quad \frac{d\alpha}{d\xi} - \frac{d^2\alpha}{d\xi^2} = 0 \quad (17)$$

$$\frac{d\beta}{d\xi} - \frac{d^2\beta}{d\xi^2} = -\Lambda_2 \beta^2 \quad (18)$$

$$\alpha + \beta + \theta = \theta_1 \quad (16)$$

$$\xi > 0 \quad \alpha = 0 \quad (19)$$

$$\frac{d\beta}{d\xi} - \frac{d^2\beta}{d\xi^2} = -\Lambda_2 \beta^2 \quad (20)$$

$$\beta + \theta = \theta_1 \quad (21)$$

The solution of (17) with the boundary condition  $\alpha(-\infty) = 1$  , ,  $\alpha(0) = 0$  is

$$\alpha = 1 - \exp \xi \quad (22)$$

Equation (18) must be solved with the boundary conditions  $\beta(-\infty) = 0$  , ,  $\beta(0) = \beta_2 = \theta_1 - \theta_2$  .

$$(23)$$



The boundary conditions for Eq.(20) are  $\beta(0) = \beta_2$  , ,  
 $\beta(\infty) = 0$ .

The concentration of b at  $\xi = 0$  is given by  $\beta_2 = \theta_1 - \theta_2$ .  
 For the complete determination of the solution we must add the  
 relation

$$\beta_{\xi}(-0) - \beta_{\xi}(+0) = 1 \quad (24)$$

obtained from the matching conditions of these outer solutions  
 with the solution of the equations describing the structure of  
 the inner first step reaction zone. These equations may be shown  
 to be

$$\frac{d^2\alpha}{d\xi^2} = \Lambda_1 \exp(-E/RT_2) \beta_2 \alpha \exp\{E(T-T_2)/RT_2^2\} \quad (25)$$

$$\alpha + \beta + \theta = \theta_1 \quad (6)$$

$$\frac{d^2\theta}{d\xi^2} = 0 \quad (26)$$

The convective effects may be neglected compared with the diffusive effects because of the small thickness of the first step reaction zone; for the same reason the effects of the second recombining reaction may also be neglected, and  $\beta$  may be written as  $\beta_2$  when evaluating the reaction rate. In addition the Arrhenius exponent may be linearized about  $T_2$ . The thickness of this



reaction zone is determined by the fact that  $E(T-T_2)/RT_2$  should not be large compared with unity.

The solution of Eq.(26) is

$$\theta = \theta_2 + p\xi, \quad (27)$$

where  $p$  has to be determined from the matching conditions with the outer solution.

Eq.(25) may now be written as

$$\frac{d^2\alpha}{d\xi^2} = \alpha\Lambda_2\beta_2 \exp \frac{Ep\xi}{RT_2\theta_2} \quad (28)$$

with the boundary conditions

$$\alpha(\infty) = 0, \quad \alpha_\xi(-\infty) = -1 \quad (29)$$

obtained from the matching conditions with the outer solutions Eq.(19) and (22). The solution is

$$\alpha = AK_0(t) \quad (30)$$

where  $t = (2\sqrt{\Lambda_2\beta_2} RT_2/Ep) \exp(\xi E/2RT_2\theta_2)$ ,  $K_0$  is a modified Bessel function of zero order, and

$$A = -2RT_2\theta_2/Ep \quad (31)$$

The matching conditions between (27) and the outer solutions of the equations (18) and (20) yield

$$p = 1 - \beta_\xi(-0) = -\beta_\xi(+0) \quad (32)$$

Let us now turn back to the solution of Eq.(18) or (20)

$$\frac{d\beta}{d\xi} - \frac{d^2\beta}{d\xi^2} = -\Lambda_2\beta^2 \quad (33)$$

to be solved for  $\xi < 0$  with the boundary conditions

$$\beta(-\infty) = 0 \quad , \quad \beta(0) = \beta_2 \quad , \quad (34)$$

and for  $\xi > 0$  with the boundary conditions

$$\beta(+\infty) = 0 \quad \beta(0) = \beta_2 \quad , \quad (35)$$

while the additional condition

$$\beta_\xi(-0) - \beta_\xi(+0) = 1 \quad (36)$$

will be used to calculate  $\Lambda_2(\beta_2)$ , and thereby the flame propagation speed.

Zeldovich (1961), when analyzing this intermediate regime for large activation energies, obtained a system of equations similar to this to describe distribution of concentration of the intermediate species. Then he proceeded with a linearization of equation (33) can not be justified.

To solve Eq.(33) we introduce the variable  $\Lambda_2\beta = \phi$  and  $y = d\phi/d\xi$  so that it takes the form

$$y - ydy/d\phi = -\phi^2 \quad (37)$$

This equation, when solved with the boundary condition

$$y/\phi = 1 \quad \text{for} \quad \phi \rightarrow 0 \quad (39)$$

which corresponds to the boundary condition  $\beta(-\infty) = 0$ , indicating that at the upstream edge of the flame convection and diffusion effects are balanced. When eq.(37) is solved with the boundary condition

$$y + \phi^2 = 0 \quad \text{for} \quad \phi \rightarrow 0 \quad (39)$$

which corresponds to  $\beta(\infty) = 0$ , it indicates a balance of the recombination and convective effects.

Let the solution of Eqs. (37) and (38) be  $y_1(\phi)$ , and  $y_2(\phi)$  the solution of Eqs.(37) and (39). Let

$$y_3(\phi) = y_1 - y_2 \quad (40)$$

The condition (36) takes the form

$$y_3 (\Lambda_2 \beta_2) = \Lambda_2 \quad (41)$$

from which it is easy to deduce the relation

$$\Lambda_2 = f(\beta_2) \quad (42)$$

giving the flame speed in terms  $\beta_2$ , and therefore in terms of  $B_1/B_2$  if Eq.(16) is taken into account.

For large values of  $\phi$

$$y_1 \doteq \sqrt{2/3} \phi^{3/2} \{1 + (\sqrt{2/3} + \sqrt{3/2})^{-1} \phi^{-1/2} + \dots\}$$

$$y_2 \doteq -\sqrt{2/3} \phi^{3/2} \{1 - (\sqrt{2/3} + \sqrt{3/2})^{-1} \phi^{-1/2} + \dots\}$$



so that

$$y_3 = 2 \sqrt{2/3} \phi^{3/2} \{1 + o(\phi^{-1})\}$$

For small values of

$$y_3 = \phi + (3/2)\phi^2 + \dots$$

The relation  $\Lambda_2(\beta_2)$  as obtained from the numerical results has been plotted in Fig.2, together with the relation

$$\Lambda_2 = (3/8)\beta_2^{-3}(1-\beta_2^2)(1+\beta_2^2/2)^{-1} \quad (43)$$

which is a very accurate analytical correlation of the numerical results, and takes into account the asymptotic representation of  $y_3$  for large and small values of  $\phi$ . The correlation (43) and the numerical results coincide within the accuracy of Fig.2.

#### 4. SLOW RECOMBINATION REACTION

We shall now analyze the case when  $\Lambda_2/\Lambda_1 = B_2/B_1 \ll \exp(-E/RT_0)$ : in this case a thick recombination region follows downstream of an isothermal autocatalytic flame. That is, in a first region, the conservation equations describing the isothermal autocatalytic flame are

$$\alpha + \beta = 1 \quad , \quad \theta = \theta_0 \quad (43')$$

$$\frac{d\beta}{d\xi} - \frac{d^2\beta}{d\xi^2} = \beta(1-\beta)\Lambda_1 \exp(-E/RT_0) \quad (44)$$

to be solved with the boundary conditions

$$\beta(-\infty) = 0 \quad , \quad \beta(\infty) = 1 \quad . \quad (45)$$

We anticipate that  $\Lambda_1 \exp(-E/RT_0)$  will be of order unity so that the thickness of this flame is of order unity in  $\xi$ . A much thicker recombination region follows downstream. Because its thickness is of order  $1/\Lambda_2 \gg 1$ , the diffusive effects turn out to be negligible in this region so that the conservation equation reduce to

$$\frac{d\beta}{d\xi} = -\Lambda_2 \beta^2 \quad (46)$$

$$\beta + \theta = \theta_1 \quad (47)$$

to be integrated with the boundary condition

$$\beta(0) = 1 \quad (48)$$

because we locate the thinner isothermal region close to  $\xi = 0$ . The solution is  $\beta = 1/(1+\Lambda_2 \xi)$ .

Zeldovich (1948) quotes the results of analysis by B.N. Skalov and O.M. Todes in 1938 and also the work of Kolmogorov, Petrovskii and Piskunov (1937), who show that a solution of Eq. (44) with the boundary conditions (45) is possible for all values of

$$\Lambda_1 \exp(-E/RT_0) \leq 1/4 \quad (49)$$

However when considering the steady flame propagation

process as the limit, for  $t \rightarrow \infty$ , of an unsteady problem, it turns out that the limiting flame propagation velocity is the minimum possible, that is

$$\Lambda_1 \exp(-E/RT_0) = 1/4 \quad (50)$$

If we write  $y = d\beta/d\xi$ , Eq.(44) takes, for the limiting value of  $\Lambda_1$ , the following form

$$dy/d\beta = 1 - \beta(1-\beta)/4y \quad (51)$$

to be integrated with the boundary condition  $y(0) = 0$ . So that for small values of  $\beta$ ,  $y = (\beta/2)(1+\beta+\beta^2/2 + \dots)$ . For values of  $\beta$  close to 1,  $y$  takes the form  $y = \{(\sqrt{2}-1)/2\}(1-\beta) + \dots$ . The isothermal chain flame structure is shown in Fig.3 where  $\beta$  has been plotted as a function of  $\xi$ .

## 5. CONCLUSIONS

We have carried out in the previous sections an analysis of the structure of a deflagration wave supported by a two step chemical reaction mechanism with a first order chain-branching reaction and a second order chain termination reaction. Three regimes have been found for large values of the activation energy of the chain branching reaction.

In a first regime. for large recombination rates, the quasi-steady approximation may be used for the intermediate species,



Eq.7, and an overall reaction rate with large activation energies describes the evolution of the temperature and concentration of the initial reactant. An explicit closed form relation, Eq.(15) has been obtained for the flame propagation velocity.

For intermediate values of the recombination rates, such that the temperature  $T_2$  obtained from Eq.(16) lies between the initial and final temperature  $T_0$  and  $T_1$ , the recombination reaction takes place everywhere in the flame. The conversion of the initial reactant into the intermediate species occurs only in a thin region where the concentration of this species  $\beta$  takes a value given in first approximation by  $\beta_2 = c(T_1 - T_2)/ha_0$ . The concentration of  $\beta$  in the much thicker recombination regions is given by Eqs. (37) with the boundary conditions Eqs.(38) and (39). That is  $\beta(\xi)$  is given by

$$\xi = - \int_{\Lambda_2^\beta}^{\Lambda_2^{\beta_2}} d\phi / y_1(\phi) \quad \text{for} \quad \xi < 0 \quad (52)$$

and

$$\xi = - \int_{\Lambda_2^\beta}^{\Lambda_2^{\beta_2}} d\phi / y_2(\phi) \quad \text{for} \quad \xi > 0 \quad (53)$$

The flame propagation velocity is in this regime very accurately

correlated by the Eq.(43).

For low recombination rates an isothermal chain reaction flame, where only the catalytic reaction occurs, moves with a velocity given by Eq (50), preceding a much thicker recombination region where  $\beta$  is given by  $\beta = 1/(1+\Lambda_2\xi)$ . The concentration profile for  $\beta$  is given in Fig.3 for the catalytic reaction region.

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LIST OF FIGURE CAPTIONS

Fig.1 Schematic of temperature and concentration profiles through the flame for the three regimes considered in the paper.

Fig.2 Functions  $y_1$ ,  $y_2$  and  $y_3$  of  $\phi$  defining the structure of the recombination regions of the flame for intermediate recombination rates. Also, the flame propagation parameter  $\Lambda_2$  in terms of the concentration  $\beta_2$  of the species  $\beta$  in the catalytic reaction zone.

Fig.3 Structure of the catalytic reaction zone of the flame for low recombination rates.

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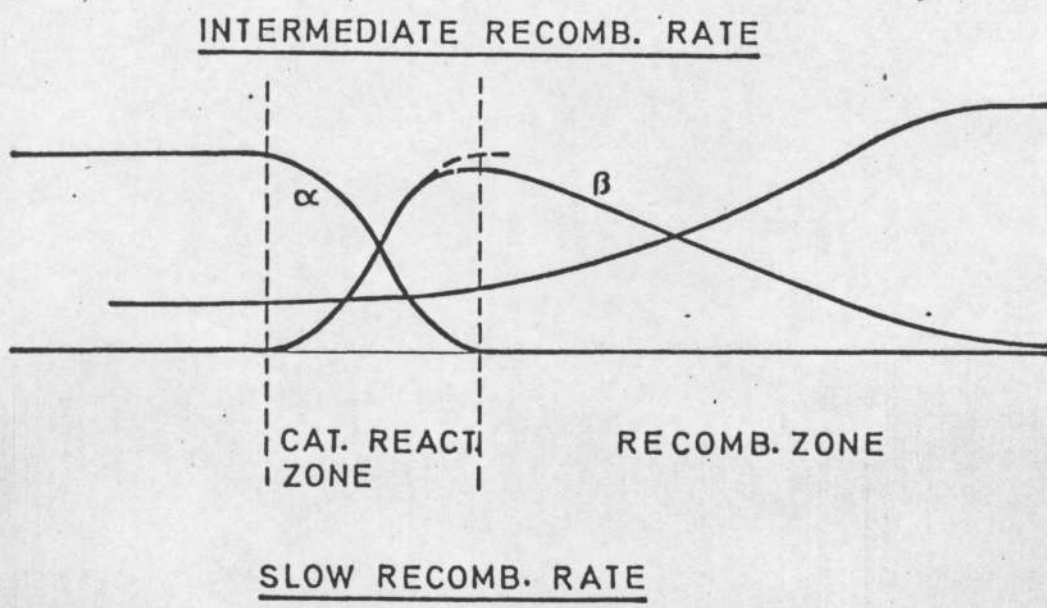
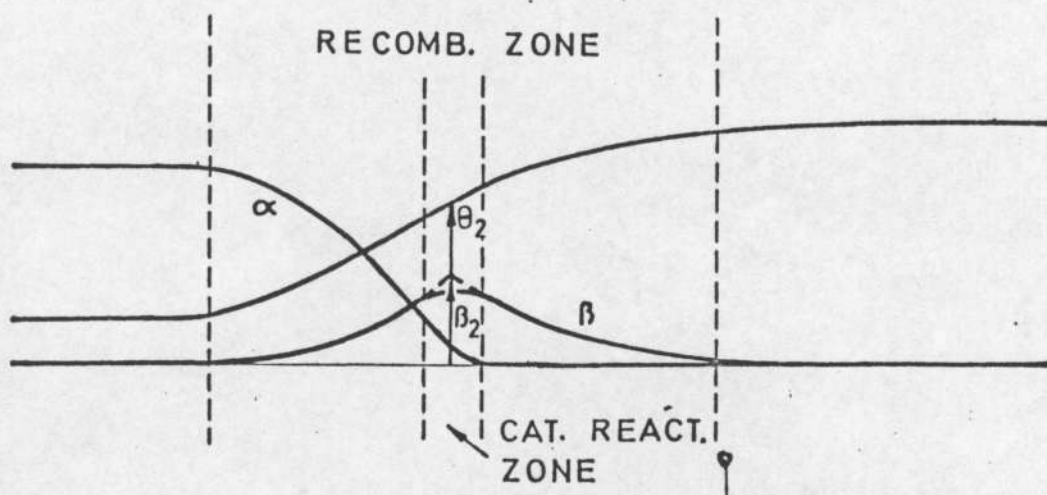
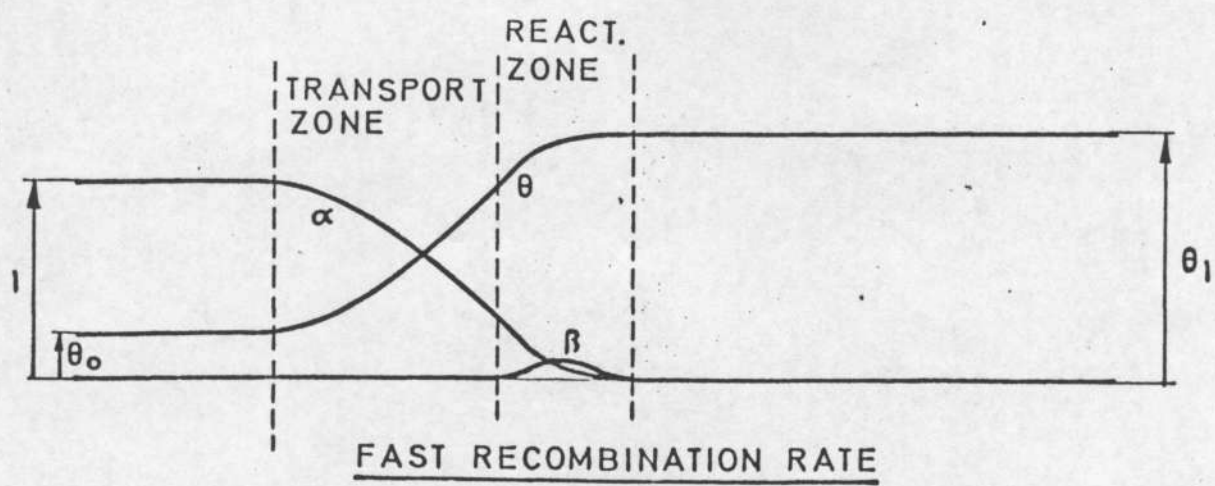


Fig. 1



Fig. 2



